

Role of Substitutional Arsenic in Pyrite Oxidation

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Introduction: There is currently much interest in the weathering of pyrite (FeS_2) and its role in acid-mine drainage. In addition, pyrite often contains significant amounts of heavy metals (As, Se, Hg, Cu, Ni, etc.) that can be released to the environment as a result of pyrite weathering. However, the role of such trace substituents on the actual mechanisms and rate of pyrite weathering has never been fully examined. Previous work [1,2] has provided indications that arsenic associated with pyrite oxidizes at a faster rate than the iron in the pyrite structure, leading to the suggestion that the mechanism and rate of pyrite weathering may be a function of the concentration of various trace metals in the pyrite structure. In order to examine these effects in more detail, a combined As XAFS spectroscopy and Fe Mössbauer study has been initiated on five bituminous coal samples containing different amounts of pyrite having differing As contents.

Methods and Materials: Aliquots of five bituminous coals having different pyrite and arsenic contents are being exposed to different conditions (air, dry argon, dry oxygen, wetted coal in air) at room temperature. At periodic intervals, the coals are being sampled and then examined by As XAFS spectroscopy and Fe Mössbauer spectroscopy to determine quantitatively the extents of the arsenic and iron oxidation. The total arsenic and pyrite contents of the coals will be determined by standard chemical analysis methods. Arsenic levels in pyrite will be confirmed by electron microprobe analysis. Arsenic XAFS spectroscopy will be used to determine the relative amounts of the unoxidized and oxidized arsenic forms in the coal. Such work is being conducted at NSLS using a multi-element Ge detector with PHA gating capability [3]. The first XAFS session for this study was conducted in October/November 2002. As of that date, the coal samples had been exposed to the different conditions for less than a month. The oxidation treatments and related spectroscopic measurements are expected to continue for up to 2 years.

Results: Qualitative examination of the As XANES spectra of the coal samples shows the presence of major peaks for arsenical pyrite, in which the arsenic oxidation state is nominally As^{-1} , and minor peaks for arsenate forms, in which the arsenic oxidation state is nominally As^{5+} . In these initial determinations, there is no compelling evidence for the presence of intermediate oxidation states of arsenic, which will simplify the quantitative analysis to be undertaken based on least-squares fitting of the As XANES spectra. Of the different atmospheres to which the coal has been exposed, only the air-wet samples showed a significant increase in As oxidation based on the initial examination of XAFS data.

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References:

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